STATIONARY SOURCE TEST METHOD

ARB Method 106: Determination of Vinyl Chloride Emissions from Stationary Sources

Introduction

Performance of this method should not be attempted by persons unfamiliar with the operation of a gas chromatograph, nor by those who are unfamiliar with source sampling, as there are many details that are beyond the scope of this presentation. Case must be exercised to prevent exposure of sampling personnel to vinyl chloride, a carcinogen.

1. Principle and Applicability

   1.1 An integrated bag sample of stack gas containing vinyl chloride (chloroethene) is subjected to chromatographic analysis, using a flame ionization detector.

   1.2 The method is applicable to the measurement of vinyl chloride in stack gases from ethylene dichloride, vinyl chloride and polyvinyl chloride manufacturing processes, except where the vinyl chloride is contained in particulate matter.

2. Range and Sensitivity. The lower limit of detection will vary according to the chromatograph used. Values reported include 1×10^{-7} mg and 4×10^{-7} mg.

3. Interferences. Acetaldehyde, which can occur in some vinyl chloride sources, will interfere with the vinyl chloride peak from the Chromasorb 1021 column. See Sections 4.3.2 and 6.4. If resolution of the vinyl chloride peak is still not satisfactory for a particular sample, then

[1] Mention of trade names on specific products does not constitute endorsement by the Air Resources Board.

chromatograph parameters can be further altered with prior approval of the Executive Officer. If alteration of the chromatograph parameters fails to resolve the vinyl chloride peak, then supplemental confirmation of the vinyl chloride peak through an absolute analytical technique, such as mass spectroscopy, must be performed.

4. Apparatus

4.1 Sampling (Figure 106-1).

4.1.1 Probe. Stainless Steel, Pyrex Glass, or Teflon Tubing according to stack temperature, each equipped with a glass wool plug to remove particulate matter.

4.1.2 Sample line. Teflon, 6.4 mim. outside diameter, of sufficient length at connect probe to bag. A new unused piece is employed for each series of bag samples that constitutes an emission test.

4.1.3 Male (2) and female (2) stainless steel quick-connects, with ball checks (one pair without) located as shown in Figure 106-1.

4.1.4 Tedlar bags, 100 liter capacity. To contain sample. Teflon bags are not acceptable. Aluminized Mylar bags may be used, provided that the samples are analyzed within 24 hours of collections.

4.1.5 Rigid leakproof containers for 4.1.4 with covering to protect contents from sunlight.

4.1.6 Needle valve. To adjust sample flow rate.

Figure 106-1 Integrated bag sampling train.

4.1.7 Pump. Leak-free. Minimum capacity 2 liters per minute.

4.1.8 Charcoal tube. To prevent admission of vinyl chloride to atmosphere in vicinity of samplers.

4.1.9 Flow meter. For observing sample flow rate: capable of measuring a flow range from 0.10 to 1.00 liter per minute.

4.1.10 Connecting tubing. Teflon, 6.4 mm outside diameter to assembly sample train (Figure 106-1).

4.1.11 Pitot tube. Type S (or equivalent), attached to the probe so that the sampling flow rate can be regulated proportional to the stack gas velocity.

4.2 Sample Recovery.

4.2.1 Tubing. Teflon, 6.4 mm outside diameter, to connect bag to gas chromatograph sample loop. A new unused piece is employed for each series of bag samples that constitutes an emission test and is to be discarded upon conclusion of analysis of those bags.

4.3 Analysis

4.3.1 Gas chromatograph. With flame ionization detector, potentometric strip chart recorder and 1.0 to 5.0 ml heated sampling loop in automatic sample valve.

4.3.2 Chromatographic column. Stainless steel, 2 m x 3.2 mm, containing 80/100 mesh Chromasorb 102. A secondary column of GE SF-96, 20 percent on 60/80 mesh AW Chromasorb P, stainless steel, 2 m x 3.2 mm or Porapak T,

80/100 mesh, stainless steel, 1 m x 3.2 mm is required if acetaldehyde is present. If used, a secondary column is placed after the Chromasorb 102 column. The combined columns should then be operated at 120° C.

4.3.3 Flow meters (2). Rotameter type, 0 to 100 ml/min capacity, with flow control valves.

4.3.4 Gas regulators. For required gas cylinders.

4.3.5 Thermometer. Accurate to one degree centigrade, to measure temperature of heated sample loop at time of sample injection.

4.3.6 Barometer. Accurate to 5 mm Hg. to measure atmospheric pressure around gas chromatograph during sample analysis.

4.3.7 Pump. Leak-free. Minimum capacity of 100 ml/min.

4.4 Calibration

4.4.1 Tubing. Teflon, 6.4 mm outside diameter, separate pieces marked for each calibration concentration.

4.4.2 Tedlar bags. Sixteen-inch square size, separate bag marked for each calibration concentration.

4.4.3 Syringe. 0.5 ml, gas tight.

4.4.4 Syringe. 50 ul, gas tight.

4.4.5 Flow meter. Rotameter type, 0 to 1000 ml/min range accurate to ± 1%, to meter nitrogen in preparation of standard gas mixtures.

4.4.6 Stop watch. Of known accuracy, to time gas flow in preparation of standard gas mixtures.

5. Reagents. It is necessary that all reagents be of chromatographic grade.

5.1 Analysis.

5.1.1 Helium gas or nitrogen gas. Zero grade, for chromatographic carrier gas.

5.1.2 Hydrogen gas. Zero grade.

5.1.3 Oxygen gas, or Air, as required by the detector. Zero grade.

5.2 Calibration. Use one of the following options: either 5.2.1 and 5.2.2, or 5.2.3.

5.2.1 Vinyl chloride, 99.9+ percent. Pure vinyl chloride gas certified by the manufacturer to contain a minimum of 99.9 percent vinyl chloride for use in the preparation of standard gas mixtures in Section 7.1. If the gas manufacturer maintains a bulk cylinder supply of 99.9+ percent vinyl chloride, the certification analysts may have been performed on this supply rather than on each gas cylinder prepared from this bulk supply. The date of gas cylinder preparation and the certified analysis must have been affixed to the cylinder before shipment from the gas manufacturer to the buyer.

5.2.2 Nitrogen gas. Zero grade, for preparation of standard gas mixtures.

5.2.3 Cylinder standards (3). Gas mixture standards (50, 10, and 5 ppm vinyl chloride in nitrogen cylinders) for which the gas composition has been certified by the manufacturer. The manufacturer must have recommended a maximum shelf life for each cylinder so that the concentration does not change greater than $\pm$ 5 percent from the certified value. The date of gas cylinder preparation, certified vinyl chloride concentration and recommended maximum shelf life must have been affixed to the cylinder before shipment from the gas manufacturer to the buyer. These gas mixture standards may be directly used to prepare a chromatograph calibration curve as described in Section 7.3.

5.2.3.1 Cylinder standards certification. The concentration of vinyl chloride in nitrogen in each cylinder must have been certified by the manufacturer by a direct analysis of each cylinder using an analytical procedure that the manufacturer had calibrated on the day of cylinder analysis. The calibration of the analytical procedure shall, as a minimum, have utilized a three-point calibration curve. It is recommended that the manufacturer maintain two calibration standards and use these standards in the following way: (1) A high concentration standard (between 50 and 100 ppm) for preparation of a calibration curve by an appropriate dilution technique; (2) a low concentration standard (between 5 and 10 ppm) for verification of the dilution technique use.

5.2.3.2 Establishment and verification of calibration standards. The concentration of each calibration standard must have been established by the manufacturer using reliable procedures. Additionally, each calibration standard must have been verified by the manufacturer by one of the following procedures, and the agreement between the initially determined concentration value and the verification concentration value must be within ± 5 percent: (1) verification value determined by comparison with a calibrated vinyl chloride permeation tube, (2) verification value determined by comparison with a gas mixture prepared in accordance with the procedure described in Section 7.1 and using 99.9+ percent vinyl chloride, or (3) verification value obtained by having the calibration standard analyzed by the National Bureau of Standards. All calibration standards must be renewed on a time interval consistent with the shelf life of the cylinder standards sold.

6. Sampling.

6.1 Procedure. Assemble the sample train as in Figure 106-1. Perform a bag leak check according to Section 7.4. Observe that all connections between the bag and the probe are tight. Place the end of the probe at the centroid of the stack and start the pump with the needle valve adjusted to yield a flow of 0.5 lpm. After a period of time

sufficient to purge the line several times has elapsed, connect the vacuum line to the bag and evacuate the bag until the rotameter indicates no flow, then reposition the sample and vacuum lines and begin the actual sampling, keeping the rate proportional to the stack velocity. Direct the gas existing the rotameter away from sampling personnel. At the end of the sample period, shut off the pump, disconnect the sample line from the bag, and disconnect the vacuum line from the bag container. Protect the bag container from sunlight.

6.2 Sample storage. Sample bags must be kept out of direct sunlight. When at all possible, analysis is to be performed within 24 hours, but in no case in excess of 72 hours of sample collection.

6.3 Sample recovery. With a piece of Teflon tubing identified for that bag, connect a bag inlet valve to the gas chromatograph sample valve. Switch the valve to withdraw gas from the bag through the sample loop. Plumb the equipment so the sample gas passes from the sample valve to the leak-free pump, and then to a charcoal tube, followed by a 0-100 ml/min rotameter with flow control valve.

6.4 Analysis. Set the column temperature to 100^{o} C, the detector temperature to 150^{o} C, and the sample loop temperature to 70^{o} C. When optimum hydrogen and oxygen flow rates have been determined verify and maintain these flow rates during all chromatograph operations. Using zero helium or nitrogen as the carrier gas, establish a flow rate in the range consistent with the manufacturer's requirements for satisfactory detector operation. A flow rate of approximately 40 ml/min should

produce adequate separations. Observe the base line periodically and determine that the noise level has stabilized and that base line drift has ceased. Purge the sample loop for thirty seconds at the rate of 100 ml/min, then activate the sample valve. Record the injection time (the position of the pen on the chart at the time of sample injection), the sample number, the sample loop temperature, the column temperature, carrier gas flow rate, chart speed and the attenuator setting. Record the laboratory pressure. From the chart, select the peak having the retention time corresponding to vinyl chloride, as determined in Section 7.2. Measure the peak area, Am, by use of a disc integrator or a planimeter. Measure the peak height, hm. Record Am, Hm and the retention time. Repeat the injection at least two times or until two consecutive vinyl chloride peaks do not vary in area more than 5%. The average value for these two areas will be used to compute the bag concentration.

Compare the ratio of Hm to Am for the vinyl chloride sample with the same ratio for the standard peak which is closest in height. As a guideline, if these ratios differ by more than 10%, the vinyl chloride peak may not be pure (possibly acetaldehyde is present) and the secondary column should be employed (see Section 4.3.2)

6.5 Measure the ambient temperature and barometric pressure near the bag. (Assume the relative humidity to be 100 percent.) From a water saturation vapor pressure table, determine and record the water vapor content of the bag.

7. Calibration and Standards.

7.1 Preparation of vinyl chloride standard gas mixtures. Evacuate a 16-inch square Tedlar bag that has passed a leak check (described in Section 7.4) and meter in 5 liters of nitrogen. While the bag is filling, use the 0.5 ml syringe to inject 250 u) of 99.9+ percent vinyl chloride through the wall of the bag. Upon withdrawing the syringe needle immediately, cover the resulting hole with a piece of adhesive tape. The bag now contains a vinyl chloride concentration of 50 ppm.. In a like manner, use the other syringe to prepare gas mixtures having 10 and 5 ppm vinyl chloride concentrations. Place each bag on a smooth surface and alternately depress opposite sides of the bag 50 times to further mix the gases. These gas mixture standards may be used for 10 days from the date of preparation, after which time preparation of new gas mixtures is required. (CAUTION. Contamination may be a problem when a bag is reused if the new gas mixture standard contains a lower concentration than the previous gas mixture standard did.)

7.2 Determination of vinyl chloride retention time. This section can be performed simultaneously with Section 7.3. Establish chromatograph conditions identical with those in Section 6.3 above. Set attenuator to X 1 position. Flush the sampling loop with zero helium or nitrogen and activate the sample valve. Record the injection time, the sample loop temperature, the column temperature, the carrier gas flow rate, the chart speed and the attenuator setting. Record peaks and detector responses that occur in the absence of vinyl chloride. Maintain conditions. With the equipment

plumbing arranged identically to Section 6.3, flush the sample loop for 30 seconds at the rate of 100 ml/min with one of the vinyl chloride calibration mixtures and activate the sample valve. Record the injection time. Select the peak that corresponds to vinyl chloride. Measure the distance on the chart from the injection time to the time at which the peak maximum occurs. This quantity, divided by the chart speed, is defined as the retention time record.

7.3 Preparation of chromatograph calibration curve. Make a gas mixture standard (described in section 5.2.2 or 7.1) using conditions identical with those listed in Sections 6.3 and 6.4. Flush the sampling loop for 30 seconds at the rate of 100 ml/min with each standard gas mixture and activate the sample valve. Record C_c, the concentration of vinyl chloride injected, the attenuator setting, chart speed, peak area, sample loop temperature, column temperature, carrier gas flow rate, and retention time. Record the laboratory pressure. Calculate A_c, the peak area multiplied by the attenuator setting. Repeat until two injection areas are within 5 percent, then plot these points v. C_c. When the other concentrations have been plotted, draw a smooth curve through the points. Perform calibration daily or before and after each set of bag samples, whichever is more frequent.

7.4 Bag leak checks. While performance of this section is required subsequent to bag use, it is also advised that it be performed prior to bag use. After each use, make sure a bag did not develop leaks as follows. To leak check, connect a water manometer and pressurize the bag to 5-10 cm H_2O (2-4 in H_2O). Allow to stand for 10 minutes.

Any displacement in the water manometer indicates a leak. Also check the rigid

container for leaks in this manner.

NOTE: An alternative leak check method is to pressurize the bag to 5-10 cm H_2O or 2-4 in. H_2O and allow to stand overnight. A deflated bag indicates a leak. For each sample bag in its rigid container, place a rotometer in-line between the bag and the pump inlet. Evacuate the bag. Failure of the rotameter to register zero flow when the bag appears to be empty, indicates a leak.

8. Calculations.

8.1 Determine the sample peak area as follows:

$$A_c = A_m A_f \qquad \text{Equation 106-1}$$

Where:

A_c = The sample peak area.

A_m = The measured peak area.

A_f = The attenuation factor.

8.2 Vinyl chloride concentrations. From the calibration curve described in Section 7.3 above, select the value of C_c that corresponds to A_c, the sample peak area. Calculate C_b as follows:

Equation 106-2 goes here.

Where:

B_{wb} = The water vapor content of the bag sample, as analyzed.

C_b = The concentration of vinyl chloride in the bag sample in ppm.

C_c = The concentration of vinyl chloride indicated by the gas

chromatograph, in ppm..

P_r = The reference pressure and the laboratory pressure recorded during calibration, mm Hg.

T_i = The sample loop temperature on the absolute scale at the time of analysis, ^oK.

P_i = The laboratory pressure at time of analysis, mm Hg.

T_r = The reference temperature and the sample loop temperature recorded during calibration, ^oK.

9. References

1. Brown, D. W., Loy, E. W. and Stephenson, M. H. "Vinyl Chloride Monitoring Near the B. F. Goodrich Chemical Company in Louisville, Kentucky." Region IV, U.S. Environmental Protection Agency, Surveillance and Analysis Division, Athens, George, June 24, 1974.

2. "Evaluation of a Collection and Analytical Procedure for Vinyl Chloride in Air," by G. D. Clayton and Associates, December 13, 1974. EPA Contract No. 68-02-1408, Task Order No. 2, EPA Report No. 75-VCL-1.

3. "Standardization of Stationary Source Emission Method for Vinyl Chloride," by Midwest Research Institute, 1976. EPA Contract 68-02-1098. Task Order No. 7.